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# A Micrographic and Gravimetric Study of Intercalation and Deintercalation of Graphite Fibers



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# A MICROGRAPHIC AND GRAVIMETRIC STUDY OF INTERCALATION AND DEINTERCALATION OF GRAPHITE FIBERS

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## SUMMARY

Intercalation and deintercalation of Union Carbide P-100 graphite fibers with liquid and vaporous bromine was studied gravimetrically and microscopically. The mass of the bromine intercalated fibers was found to be 17 to 20 percent greater than their pristine counterpart. This variation decreased to 17 to 18 percent after heating in air for 3 days at 200 °C and 14.5 to 18 percent after 6 days of 260 °C heating. The fiber length did not change throughout the experiment. The fiber diameter increased during intercalation and decreased slightly upon deintercalation but was not affected by heating to 260 °C for 3 days in air. Comparing the mass and volume data to those with HOPG or natural single crystal graphite suggested the possibility that the intercalated P-100 fibers could be mostly stage 4.

## INTRODUCTION

Graphite fibers are currently of interest for aerospace applications requiring light-weight, high-strength materials. With intercalation, where guest materials are introduced into graphite to form ordered layered structures in between graphite planes, certain physical properties critical for some applications can be improved. For example, after intercalation in bromine atmosphere and then deintercalation in air, the conductivity of Union Carbide P-100 graphite fibers is 5 times its unintercalated value (ref. 1). Thus, bromine intercalated P-100 graphite fiber-epoxy composites could be a strong, light-weight material for spacecraft electronic boxes which must also provide electromagnetic interference shielding or as a material for aircraft surface which require lightening strike survivability.

The objectives of the research reported in this paper was to determine whether graphite fibers can be uniformly intercalated at macroscopic and microscopic levels, to determine the composition of the intercalated fibers and, from the mass and volume data to find the relationship between intercalated P-100 graphite fibers and intercalated natural crystals or intercalated HOPG (highly oriented pyrolitic graphite) whose properties have been widely studied.

The macroscopic uniformity of intercalation was evaluated by determining the bromine content of fiber sections cut out from different locations of 11 m intercalated fiber strands wrapped in multiple layers on a spool. The bromine content was calculated by measuring the mass increases of these fiber sections during intercalation. The calculated values were then used to determine if bromine could penetrate into the fiber spool completely and uniformly. Bromine

contents of fibers strand of different lengths and quantities were also determined by weighing before and after intercalation, deintercalation and subsequent heating. The data thus obtained could reveal if all fibers were intercalated to the same degree regardless of fiber length and quantity. Diameter and lengths of individual fibers were measured during intercalation, deintercalation and subsequent heating to determine the volume change during intercalation and the microscopic uniformity of individual intercalated fibers. Results of this report may be of assistance in determining an industrial procedure to manufacture high quality bromine intercalated P-100 graphite fibers suitable for intercalated graphite-epoxy composites whose physical properties have to be uniform and well characterized.

## EXPERIMENTAL PROCEDURE

### Bromine Consumption of a Strand of Fibers during Vaporous Bromine Intercalation

A preweighed strand of P-100 fibers (2000 fibers per strand), about 11 m long, was wound on a glass mandrel (diam 5.5 cm) such that the fiber layer wrapping the spool was 1 mm thick and less than 0.75 cm wide. It was placed in saturated bromine vapor for 2 days at room temperature and then taken out of the bromine environment. The glass chamber containing the saturated bromine vapor was pre-evacuated by a vacuum pump to about 1 mm Hg pressure. The mass of the fibers was measured before bromination. It was measured again after both 1 and 14 days of air exposure. Five 30 cm long sections were cut out of the strand of fibers including both ends and three middle sections at 2.74, 5.49 and 8.23 m from the outside end of the spool. Knowing that a strand of pristine P-100 graphite fibers has a mass of 0.0030 g/cm of fiber strand, the mass increase of these five sections was calculated based on the measured mass/length increase.

### Bromine Consumption of Long, Short, and Ground Fibers During Vaporous Bromine Intercalation

Seven samples of different fiber length were intercalated for 60 hr in bromine vapor. These samples were: a strand of fibers 168 m long wound on a 10 cm diameter spool such that the fibers made a layer less than 1 mm thick and 10 cm wide, two strands cut into 7.6 cm long segments (both in test tubes), two strands cut into 0.36 cm long segments (in either a beaker or a test tube) and two ground samples (in either a flask or a test tube). The ground fibers were obtained by grinding a strand of fibers in a test tube with a glass rod for 15 min. Microscopic inspection of the ground fibers showed that 75 percent were less than 90 μm in length. All samples were intercalated in room air saturated with bromine vapor except for the 168 m strand, which absorbed all available bromine in the chamber. The mass of all samples was measured several times during the 10 days after the intercalation period. After 3 months of air exposure, the samples were heated to 200 °C for 3 days and 260 °C for 6 days. The mass of all samples was measured again before and after the heatings.

## Bromine Consumption of a Strand of Fibers During Liquid Bromine Intercalation

Intercalation and deintercalation of P-100 graphite fibers with liquid bromine were also studied to estimate the changes ir graphite fibers under extreme conditions.

An 11 m long fiber strand was weighed and wound on a 5.5 cm diameter mandrel. The fiber layer on the spool was 2 cm wide and less than 1 mm thick. It was immersed in liquid bromine for 24 hr at room temperature and then taken out of the bromine environment. The mass of the fibers was measured before bromination. It was measured again after 1 day of air exposure. Four 30 cm long segments were then cut out of the strand of fibers including both ends and two middle segments at 3.66 and 7.32 m from outside end of the spool. Again, knowing the pristine mass to length ratio, the mass increases of these four sections was calculated. These four sections were then stored in room air for 6 months and then heated in air at 260 °C for 3 days. The mass of these four sections was measured again before and after heating.

## Diameter and Length Measurement During Liquid Bromine Intercalation and Deintercalation

One section of a single P-100 fiber was placed in a glass tube. The tube was 3 mm inside diameter, 5 mm outside diameter, 18 cm long and had one open end. Using an optical microscope, the diameter and length of this chopped fiber (in the glass tube) were measured. The microscope was a Bausch and Lomb MicroZoom microscope. A Polaroid camera was set such that the magnification could range from 18 to 390.

After introducing liquid bromine into the glass tube, it was immediately sealed by a rubber stopper and placed under the microscope for <u>in situ</u> observation. Direct contact between the chopped fiber and liquid bromine was observed, shown in figure 1. Microscopic pictures were taken after a few minutes to record the diameter and length changes. The experiment was conducted twice. Intercalation times were 50 and 140 min for the two experiments.

After intercalation was considered complete, the liquid bromine was removed from each tube. The fiber diameters and lengths after 30 hr of deintercalation were measured again. The fibers were then heated to 260 °C for 60 hr. Final fiber diameter and length measurements were then obtained.

## Diameter and Length Measurement During Vaporous Bromine Intercalation

A small amount of liquid bromine was introduced into a glass tube similar to that described in the above experiment. Several chopped fibers were then placed near the open end of the tube. After sealing the open end of the tube with a rubber stopper, the tube was immediately placed under the microscope for single fiber diameter and length measurement. One chopped fiber in the tube was selected for this purpose. After 23 hr of intercalation, the

microscope stage position was changed and diameters of seven other fibers were measured.

## RESULTS AND DISCUSSION

The mass of the 11 m long fibers intercalated with vaporous bromine was 19.3 percent heavier than its pristine value after 1 day of room temperature air exposure. The same mass was observed after 14 days of air exposure. The mass increases of the five sections cut out from this fiber strand were (from outside end to inside end of the spool): 18.3, 18.9, 20.8, 17.8 and 20.8 percent.

The mass of the 11 m long fibers intercalated with liquid bromine was 20.2 percent heavier than its pristine value after 1 day of room temperature air exposure. The mass increases of the four sections cut out from this fiber strand were (from outside end to inside end of the spool): 17.8, 19.0, 22.1 and 19.2 percent. After 6 months of air exposure, these values decreased to 17.6, 18.5, 19.8 and 18.8 percent, respectively. After 260 °C heating in air for 3 days, these values further decreased to 15.3, 16.3, 17.6 and 16.2 percent, respectively.

The increases in mass measured at different locations along the 11 m long fibers ranged from 17.8 to 20.8 percent for fibers intercalated by vaporous bromine and allowed to deintercalate for 2 weeks in air, and 17.8 to 22.1 percent for fibers intercalated by liquid bromine and allowed to deintercalated for 1 day in air. This suggested that bromine penetrated through and reacted with the whole spool of fibers, but the distribution of bromine was not uniform. These results are significant because they show that large quantities of bromine intercalated P-100 fibers can be produced in spool form if its thickness was about 1 mm or less. However, further work is needed to improve the uniformity of bromine content, although it was observed that prolonging deintercalation time or 200 °C heating could do this to some degree. The results show that both vaporous and liquid bromine intercalate to the same degree in P-100 fibers if the intercalation reaction is allowed to proceed to completion.

Figure 2 shows the mass of the 168 m fiber sample and a ground fiber sample for the first 105 min of bromine desorption. Table I summarizes the mass values of all seven samples over a 3 month of bromine desorption period and before and after heatings.

For liquid bromine intercalation, the fiber length was found to remain unchanged within 0.5 percent throughout the experiments. The diameter increased to a plateau within 10 min after the start of the intercalation, decreased during deintercalation in air at room temperature, and, in most cases, remained unchanged within 2 percent when heated to 260 °C for 2.5 to 3 days. For vaporous bromine intercalation, no fiber length change could be observed during intercalation. The fiber diameter also remained unchanged for the first several hours, but was found to be 8.8 percent larger than its parent pristine fiber after 23 hr of intercalation. Table II summarizes the diameters of intercalated and room-temperature deintercalated single fibers. It was noted that a small portion of the deintercalated fibers showed some irregularities.

The above results were examined as follows:

1. By examining the mass data for liquid bromine intercalated fiber strand and mass data presented in figure 2 and table I, it can be observed that the mass of bromine remaining in these strands of fibers asymptotically approached a value within or slightly below the range of 16.9 to 19.4 percent except for the sample of 0.36 cm fibers in a beaker. This exception may be due to loss of small fibers from the open beaker during 3 months of storage. This range of values compares favorably with the range of values reported from the analysis of the 11 m strands. The average value of 18.6 percent corresponds to an atomic ratio of $C_{71.6}Br_2$.

It is known that the greater the amount of bromine intercalated, the higher the bromine content in the residue compound (ref. 2). Since the mass of bromine remaining in the liquid bromine intercalated 11 m fiber strand and the seven samples described in table I all asymptotically approached to a value in a small range, it was concluded that they intercalated to the same compound before deintercalation process started.

2. The increase in mass due to bromine intercalation plus bromine condensation on the fiber surface at the end of the intercalation period was 50 percent for long fibers (168 m) and more than 61 percent for ground fibers. The increase in mass due to intercalation alone was believed to be the same for both sample, as explained in the last paragraph. Thus the difference in mass increase observed initially between these two samples is believed to be due to different degrees of bromine condensation on fiber surface. Bromine condensation was considered obvious because of the strong affinity between P-100 fibers and bromine, as shown in figure 1. The amount of mass increase due to intercalation alone was not known. However, it was believed to be equal or higher than the highest bromine content for fibers described in the last paragraph and exposed in air for at least 1 day. That was 22.1 percent from a middle section of the liquid bromine intercalated 11 m fiber strand.

3. After heating the vaporous bromine intercalated long, short, and ground fibers at 200 °C for 3 days, the mass of all samples approached a narrow range (17.0 to 18.1 percent heavier than the pristine values, or $C_{74-78}Br_2$) except, as described earlier in this report, the sample of 0.36 cm fibers in a beaker (14.2 percent). Subsequent heating at 260 °C for 6 days enlarged the bromine content range again, as shown in table I. This probably indicated that a new deintercalation mechanism functioning at this temperature, and that more than 6 days at 260 °C were needed to complete deintercalation via this mechanism.

Because the electric conductivity of vaporous bromine intercalated P-100 fibers is not affected by heating to 200 °C (ref. 3), the mass decreases during the heating to 200 °C must be due mostly to reasons other than bromine loss. In fact, after the completion of heating of the 49.5 gm fiber sample, some moisture was found condensed on the reactor. Thus water evaporation when heating to 200 °C is considered the major reason for mass decreases. It was also reported (ref. 3) that bromine intercalated P-100 fibers gradually lose electrical conductivity at 250 °C (ref. 3). This agrees with the results described in the previous paragraph.

4. In table II there are two data points that show extraordinary large diameters. One is for a vaporous bromine intercalated fiber, 15.1 μm diameter. The other is one end of a liquid intercalated fiber, 14.9 μm. This may be due to formation of lower stage structure or large spaces between crystallites in the graphite fibers being occupied by bromine. Exfoliation was considered unlikely since upon heating, the 14.9 μm diameter fiber section was reduced to 12.8 μm.

It was noted that the 14.9 μm diameter bromine rich fiber section could exist after 1 day of air exposure. However, it was sensitive to 260 °C heat.

5. Bardhan et al. (ref. 4) reported that the bromine content in HOPG residue compound could stay at 43.3 percent at room temperature for some time but dropped to 19 percent at 50 to 90 °C and went below 18 percent at 110 to 140 °C. In the present report, debromination of P-100 at room temperature reached completion at about 18.6 percent. It seemed that the bromine intercalated P-100 was to some degree similar to the intercalated HOPG, but has a much more active desorption area. Therefore high temperature was needed to drive out bromine trapped in the HOPG used by Bardhan et al. (4.5 to 8 mm diam, 0.1 to 0.4 mm thick disk).

6. Eeles and Turnbull (ref. 5) used several natural graphite crystal disks, 1.0 mm in diameter and 0.1 mm thick, to measure the graphite weight changes during bromine intercalation and desorption. They reported that graphite fully saturated with bromine desorbed and resulted in a quasi-stable stage 4 intercalated compound which was 24 percent heavier than the initial unbrominated graphite crystals. From their x-ray data, the volume of this compound was calculated and it was found to be 26.9 percent larger than the initial unbrominated crystal. It was also noted that for stage 2 brominated graphite, the volume was 55 percent larger than the pristine crystals. For P-100 fibers, knowing that there were void spaces between the crystallites in the fibers to accommodate the crystalline volume increase, and knowing that densities for P-100 and graphite single crystals were 1.99 (ref. 1) and 2.24, respectively, the minimum volume of homogeneous stage 2 and stage 4 brominated fibers can be calculated. They were 37.7 and 12.7 percent larger than their pristine values, respectively.

As suggested earlier in this report, the bromine content of the intercalated P-100 fibers was equal or greater than 22.1 percent of pristine weight before deintercalation started. Also, the diameters of three fibers (two intercalated with liquid bromine and one with vaporous bromine) before and after intercalation were used to calculate their volume increase. The calculated values were 23.9, 26.3 and 18.5 percent, respectively. Thus according to mass and diameter data alone, the brominated P-100 fibers could not possibly be a homogeneous stage 2, but could be a stage 4 compound. The possibility of having a stage 3 compound was not known.

Finally, the quasi-air stable 14.9 μm diameter small section described earlier in this report had a volume increase of 67.9 percent if its pristine diameter was 11.5 μm, the same as the majority part of the fiber. If diameter increases are an indicator, then this small section was possibly a stage 2 compound.

## CONCLUSIONS

Intercalation and deintercalation of Union Carbide P-100 fibers with liquid and vaporous bromine was studied gravimetrically and microscopically. Bromine contents of fiber strands of different quantities were determined by weighing before and after intercalation, deintercalation and subsequent heating. Diameters and lengths of single fibers were measured during intercalation, deintercalation and subsequent heating. From the results the following conclusions can be reached:

1. Both liquid and vaporous bromine can penetrate and react with whole spools of fibers if the thickness of the fibers wrap on the spool is 1 mm or less.

2. By supplying excessive amount of liquid or vaporous bromine and letting the intercalation reaction reach completion, bromine could react with various quantities of P-100 fibers to form the same compound.

3. Compared to intercalation of P-100 graphite fibers by liquid bromine, vaporous intercalation required less deintercalation time, generated less bromine waste and therefore was considered a more attractive intercalation technique for industrial application.

4. The weight of fibers deintercalated at room temperature was 17 to 20 percent heavier than their pristine values.

5. Heating room-temperature-deintercalated fibers to 200 °C for 3 days in air resulted in fibers 17 to 18 percent heavier than its pristine values. This small variation in percent weight gain implies that 200 °C could be an ideal posttreatment temperature if bromine content uniformity is important. The bromine content of these rather uniform P-100 fibers indicates a graphite intercalation compound of $C_{74-78}Br_2$. The variation in percent weight gain was enlarged if the fibers were further heated at 260 °C in air for 6 days.

6. The P-100 fiber diameter increased by 8 to 12 percent during intercalation, lost some of this increase during deintercalation in air at room temperature and was not affected by subsequent 260 °C heating in air. The observed fibers were mostly uniform in diameter except some irregular points which had more expansion during intercalation which was lost during 260 °C heating.

7. There were no fiber length changes upon intercalation of the fibers.

8. Brominated P-100 fibers and brominated HOPG behaved similarly, except that the temperature needed to drive out bromine trapped in HOPG was higher than that needed for P-100 fibers.

9. Mass and diameter data suggest that intercalated P-100 fibers could be a homogeneous stage 4 compound but could not be a homogeneous stage 2 compound. However, the small fiber sections with extraordinarily large diameter were possibly a stage 2 compound.

## REFERENCES


1. J.R. Gaier and D. Marino. To be presented on 17th Biennial Conference on Carbon. American Carbon Society. University of Kentucky, Lexington, KY. June 1985.

2. G. Hennig. The Journal of Chemical Physics, Vol. 20, No. 9, p. 1438. September 1952.

3. J.R. Gaier. NASA Technical Memorandum 86859.

4. K.K. Bardhan, J.C. Wu, J.S. Culik, S.H. Anderson and D.D.L. Chung. Synthetic Metals. Vol. 2, p. 57, 1980.

5. W.T. Eeles and J.A. Turnball. Proc. R. Soc. London. Ser. A, Vol. 283, p. 179, 1965.

TABLE I. - WEIGHT OF INTERCALATED FIBERS IN PERCENT OVER THE PARENT PRISTINE FIBERS DURING DESORPTION

[M = Mandrel; T = Test tube; B = Beaker; F = Flask.]

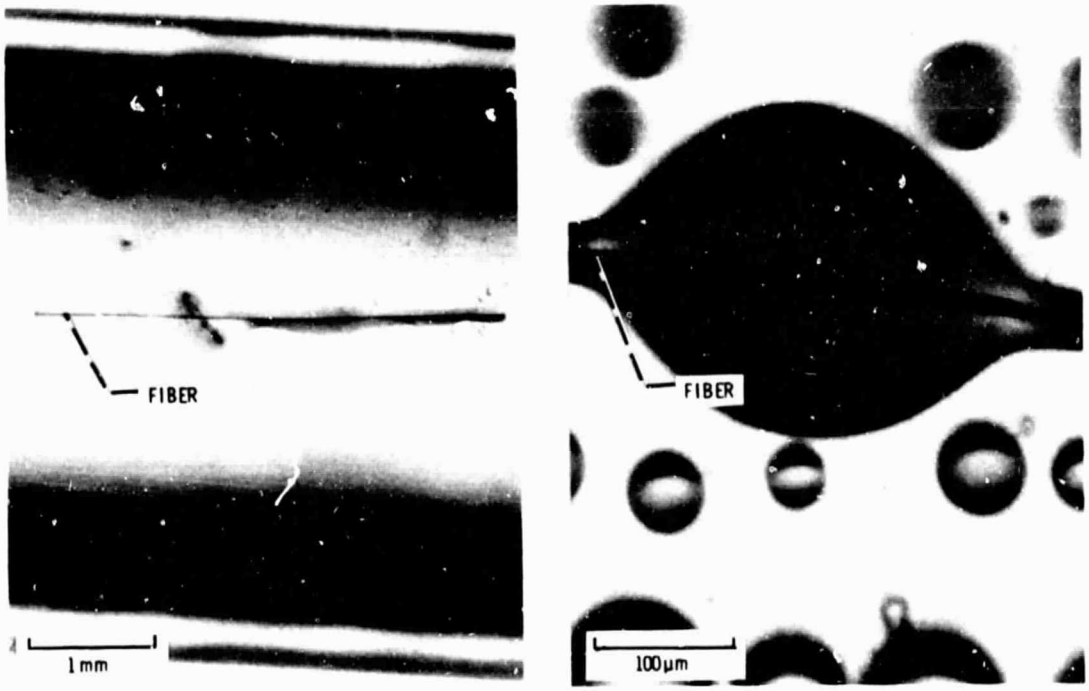
| Time | Approximate length of fiber samples | | | | | | |
|---|---|---|---|---|---|---|---|
| | 168 m | 7.6 cm | | 0.36 cm | | Ground | |
| | Approximate weight of fiber samples, gm | | | | | | |
| | 49.5 | 0.28 | 0.28 | 0.23 | 0.16 | 0.61 | 0.61 |
| | Mass increase (percent) over the pristine values | | | | | | |
| | M | T | T | B | T | F | T |
| 1.66 hr | 20 | ---- | ---- | ---- | ---- | 36.3 | ---- |
| 4.25 | ---- | ---- | ---- | 18.5 | 27.4 | ---- | ---- |
| 5.25 | 20 | ---- | ---- | ---- | ---- | ---- | ---- |
| 8 | ---- | ---- | ---- | ---- | ---- | 22.4 | ---- |
| 20 | ---- | 19.4 | 19.7 | ---- | ---- | 19.7 | 19.3 |
| 23 | ---- | ---- | ---- | 18.3 | 16.7 | ---- | ---- |
| 48 | ---- | 19.5 | 19.7 | ---- | ---- | 19.4 | 19.0 |
| 168 | 18.3 | ---- | ---- | 17.1 | 16.7 | ---- | ---- |
| 240 | 18.2 | 19.1 | 19.5 | ---- | ---- | 18.8 | 18.7 |
| 3 months | 18.3 | 19.2 | 19.4 | [a]13.8 | 16.9 | 19.0 | 18.7 |
| 200 °C/3 days | 17.0 | 17.9 | 18.1 | [a]14.2 | 17.1 | 17.8 | 17.7 |
| 260 °C/6 days | ---- | 17.6 | 17.8 | [a]11.5 | 14.5 | 17.0 | 16.9 |

[a]These low values were probably due to some fiber loss during the 3 month storage time.

TABLE II. - EFFECTS OF INTERCALATION, DEINTERCALATION AND SUBSEQUENT HEATING ON P-100 FIBER DIAMETER

| Bromine state | Number of individual fibers | Sections of individual fibers | Fiber diameter (μm) | | | |
|---|---|---|---|---|---|---|
| | | | Pristine | After intercalation in bromine environment | After deintercalation at room temperature in air for 30 hr | After 260 °C heating in air for 60 hr |
| Liquid | 1 | Majority | 11.5 | 12.8 | 12.6 | 12.6 |
| | | One end | ---- | ---- | 14.9 | 12.8 |
| | | Other end | ---- | ---- | 11.5 | 11.5 |
| | | (a) | ---- | ---- | 13.1 | ---- |
| Liquid | 1 | Majority | 12.1 | 13.6 | 12.6 | 12.7 |
| | | One end | 12.6 | 13.6 | 12.8 | 12.8 |
| | | Other end | 12.1 | 13.6 | 12.7 | 12.8 |
| Vapor | 1 | --------- | 11.3 | 12.3 | ---- | ---- |
| Vapor | 7 | --------- | ---- | [b]10.1-15.1 | ---- | ---- |

[a]An irregular point at the central portion of the fiber.
[b]Diameters of these seven fibers were: 10.1, 10.7, 11.0, 11.2, 12.0, 12.5, and 15.1 μm.




(a) Low magnification

(b) High magnification

Figure 1. - Direct contact between P-100 fibers and liquid bromine during intercalation.

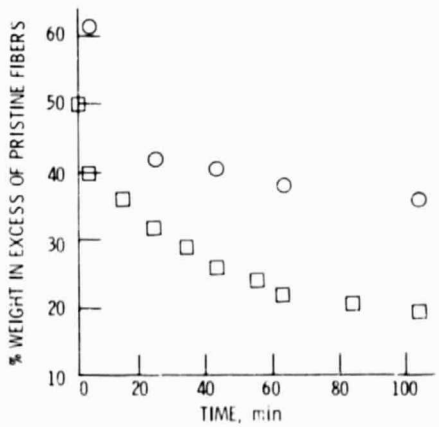



Figure 2. - Weight of intercalated fibers during the first 105 minutes after removal from the bromine intercalation environment to air ○ ground fibers, □ 168 m fiber sample.

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16. Abstract

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